

Classical Path Equations in Molecular Collisions¹

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Derivation of the classical path equations from the time-dependent Schrödinger equation is presented. Correction terms are discussed and a variational principle is shown to account for most of the missing quantum correlation.

KEY WORDS: classical path; Gaussian wave packet; quantum correlation; time-dependent self-consistent field.

1. INTRODUCTION

In order to solve the dynamics for large, i.e., many-particle, systems, it is necessary to introduce approximations. In the case of nuclear dynamics we obviously have the possibility to think in terms of a classical mechanical description of the motion. However, in spite of the heavy masses of nuclei, there remain certain number of quantum effects which have to be dealt with in the proper way, namely, quantum mechanically. Quantum effects are, e.g., connected to nonadiabatic electronic coupling (breakdown of the Born–Oppenheimer approximation), geometric phase effects [1], zero-point vibrational energy, resonances, and tunneling. It is therefore necessary to formulate a theory in which the quantum aspects can be incorporated if deemed necessary but which is also able to take advantage of the fact that much of the dynamics is well described using classical mechanics. Such a theory (called the classical path theory) has been formulated for inelastic and reactive scattering over the last decades (see Ref. 2). In the present paper we discuss some of the foundations of the theory.

The theory has been used to calculate transport properties for heavy diatomics at high temperatures [3, 4] and energy transfer in diatomic and polyatomic molecules [2]. In these calculations all the vibrational degrees of

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freedom are usually quantized, whereas translational and rotational motion were treated classically. Recently the methodology has been extended also to reactive scattering using hyperspherical variables [5].

The classical path theory can be derived from the time-dependent Schrödinger equation (TDSE) by assuming that the trial wavefunction can be written in a product form and assuming that the wavefunction remains gaussian in some degrees of freedom. The introduction of the Gaussian wavefunction gives a set of classical equations of motion for the motion of the center of the wavepacket. It is possible to correct for the gaussian approximation by introducing a correction wavefunction (Φ_{corr}). Furthermore, a variational principle in the initial parameters improves the results obtained with the simple product-type wave function. The variational principle yields a best trajectory which has turned out to be close to the one obtained using the average trajectory approach suggested many years ago (see, e.g., Ref. 2). If this search for the best trajectory is not introduced, then the ordinary or common trajectory classical path method arises. Below we discuss these points and theories further.

2. THEORY

If we, for simplicity, consider a system with just two degrees of freedom, r and R , we can quite generally expand the wavefunction as

$$\Psi(r, R, t) = \sum_n \phi_n(r) C_n(R, t) \quad (1)$$

where $\phi_n(r)$ is a suitable basis set, e.g., the eigenstates of part of the hamiltonian. We shall seek a particular solution to the TDSE, where we assume that

$$C_n(R, t) = a_n(t) X(R, t) \quad (2)$$

where normalization of the wavefunction requires that

$$\sum_n |a_n(t)|^2 = 1 \quad (3)$$

$$\int dR |X(R, t)|^2 = 1 \quad (4)$$

The Hamiltonian operator can generally be written as

$$\hat{H}(r, R) = \hat{H}_0 - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V(r, R) \quad (5)$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + v(r) \quad (6)$$

and the basis functions $\phi_n(r)$ can be chosen to be eigenfunctions to \hat{H}_0 with eigenvalues E_n . We now use Eq. (2) when inserting Eq. (1) in the TDSE. For later use we also expand the potential $V(R, r)$ as

$$V(R, r) = V(R(t), r) + \sum_{p=1} \frac{1}{p!} \left. \frac{\partial^p V}{\partial R^p} \right|_{R=R(t)} (R - R(t))^p \quad (7)$$

where $R(t)$ is a so far unspecified reference path.

We then get

$$\begin{aligned} & ih \left(\frac{da_m}{dt} X(R, t) + a_m \frac{\partial X}{\partial t} \right) \\ &= E_m a_m X(R, t) - \frac{\hbar^2}{2\mu} a_m(t) \frac{\partial^2 X(R, t)}{\partial R^2} + X(R, t) \\ & \times \left[\sum_n a_n(t) \langle \phi_m | V(r, R(t)) | \phi_n \rangle + \sum_{n, p=1} a_n(t) \frac{(R - R(t))^p}{p!} V_{nm}^{(p)} \right] \quad (8) \end{aligned}$$

with

$$V_{nm}^{(p)} = \langle \phi_m | \left. \frac{\partial^p V(R, r)}{\partial R^p} \right|_{R=R(t)} | \phi_n \rangle \quad (9)$$

Multiplication from the left with $X(R, t)^*$ and integration over R gives us

$$\begin{aligned} ih \dot{a}_m + a_m \int dR X^* \frac{\partial X}{\partial t} &= E_m a_m - \frac{\hbar^2}{2\mu} a_m \int dR X^* \frac{\partial^2 X}{\partial R^2} \\ &+ \sum_n a_n \langle \phi_m | \int dR X^* V(R, r) X | \phi_n \rangle \quad (10) \end{aligned}$$

where $\langle \rangle$ indicate integration over r . If we instead multiply by a_m^* and sum over m , we obtain

$$\begin{aligned} ih \left(\sum_m a_m^* \dot{a}_m X + \frac{\partial X}{\partial t} \right) &= X \sum |a_m|^2 E_m - \frac{\hbar^2}{2\mu} \frac{\partial^2 X}{\partial R^2} \\ &+ X \sum_{mm} a_m^* a_n \langle \phi_m | V(r, R) | \phi_n \rangle \quad (11) \end{aligned}$$

The above set of equations is those arising from the time-dependent self-consistent field (TDSCF) treatment of the problem. We notice that no reference path $R(t)$ appears in the equations, that the method can be extended to any number of degrees of freedom, and that the multidimensional problem would be reduced to a set of one-dimensional ones.

We now deviate from this scheme in a rather important fashion, namely, by introducing a reference path $R(t)$ [the center of a Gaussian wave packet (GWP)] such that

$$V(R, r) = V(R(t), r) + \Delta V \quad (12)$$

and define the expansion coefficient a_m by the equation

$$i\hbar \dot{a}_m(t) = E_m a_m(t) + \sum_n a_n(t) V_{mn}^{(0)}(R(t)) \quad (13)$$

These equations are the so-called "classical path" equations for a_n . Inserting this in Eq. (8), we obtain

$$i\hbar \frac{\partial X}{\partial t} = \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \sum_{mm} a_m^* a_n (V_{mm}(R, t) - V_{mm}(R(t), t)) \right] X(R, t) \quad (14)$$

We are allowed to do so because we have introduced two functions, $a_n(t)$ and $X(R, t)$, instead of one, $C_n(R, t)$. However, we have introduced a separability approximation in the coordinates r and R . That is, we have assumed

$$\psi(r, R, t) = X(R, t) \Phi(r, t) \quad (15)$$

i.e., a Hartree-type wavefunction. This approximation is exact only if the interaction potential can be written as $V(r, R) \sim V_1(r) + V_2(R)$. Thus the correlation between the two degrees of freedom prevents the solution in terms of the simple product wavefunction. In the TDSCF treatment given above, the correlation is treated approximately, the r -degree of freedom feels an average force over the R -coordinate, and the R -degree an average of the r -system.

The reason for introducing the reference path $R(t)$ the way it is done (see also below) is that we obtain classical equations of motion for $R(t)$. In the limit of large quantum numbers, masses, etc., we know that a classical description is correct and also, from a numerical point of view, much easier to solve than the quantum counterparts. In this (classical) limit we have a correlation, i.e., interaction, between the degrees of freedom described classically and correctly in the "classical sense."

We now apparently have a paradox—in order to derive the classical limit by introducing a GWP we have to invoke a product-type wavefunction which neglects the correlation (in the quantum sense). However, the TDSCF treatment does include the correlation, but in an average fashion. This must then mean that the Hartree product wave function

$$\Phi_{\text{GWP}}(r, t) \Phi_{\text{GWP}}(R, t) \quad (16)$$

becomes a more and more correct description in the classical limit. Or, in other words, the classical correlation is the limit the average one introduced in the TDSCF treatment when a GWP is assumed. Thus the Hartree-product trial function and the classical limit are, in a way, interrelated.

If we have two degrees of freedom, where one is described “classically” by a GWP and the other quantumly, then the correlation included between the degrees of freedom is what could be called “classical.” Here we denote by “classical” a theory where the average quantum correlation is introduced (through a GWP) and a set of classical equations of motion is obtained for the motion of the center of the GWP.

Thus the solution to the equation for $X(R, t)$ can now be introduced in such a way that the classical path equations arise as the limit of the solution. But before this is done we use the above equations to obtain the best possible values with the product-type wavefunction for a simple test system also investigated previously.

Initially $X(R, t)$ is set equal to a GWP,

$$X(R, -t) = \left(\frac{2 \operatorname{Re} A(-t)}{\pi h} \right)^{1/4} \times \exp \left(\frac{i}{h} (A(-t)(R - R(-t))^2 + P(-t)(R - R(-t))) \right) \quad (17)$$

at $-t$. $A(t)$ is the width parameter, which is parameterized at the turning point for the trajectory $R(t)$ such that, at the turning point, where $P(0) = 0$, we have $\operatorname{Im} A(0) = \alpha_0$ and $\operatorname{Re} A(0) = 0$ (see Ref. 6). $R(-t)$ is set to a large value where the interaction is vanishing. The GWP is an exact solution of Eq. (8) if the interaction potential is at most quadratic in R . This is of course the case initially, where the interaction potential vanishes. Otherwise the GWP trial function will be an approximation.

If the GWP approximation at all times is not introduced, then the only approximation is the one connected to the product-type wavefunction assumed above.

In order to determine the transition probability from an initial state I to a final state F , we set $a_n(-t) = \delta_{nI}$ and project the wavepacket $X(R, -t)$ on incoming plane waves

$$X(R, -t) = \frac{1}{\sqrt{2\pi}} \sum_n c_n^{\text{in}} \exp(-ik_n R) \quad (18)$$

where

$$\frac{\hbar^2 k_n^2}{2\mu} = E - E_n \quad (19)$$

Likewise with the scattered wavefunction—it is expanded on outgoing waves

$$X(R, t) = \frac{1}{\sqrt{2\pi}} \sum_n c_n^{\text{out}} \exp(ik_n R) \quad (20)$$

Thus the transition probability is given as

$$P_{I \rightarrow F} = \frac{k_F}{k_I} |a_F(t)|^2 \frac{|c_F^{\text{out}}|^2}{|c_I^{\text{in}}|^2} \quad (21)$$

This projection on plane waves to get the incoming and outgoing fluxes is the standard way of transforming from a time-dependent to a time-independent picture. If this projection is made, the probabilities are independent of the position in momentum space of the wavepacket, i.e., independent of $P(-t) = P_0$ and of the width parameter α_0 . A single wavepacket, in principle, covers an infinite energy range. However, when the product form of the trial function is assumed throughout the collision, then the probabilities will in general not be independent of the two parameters. This led us to suggest the following variational approach: the best initial momentum P_0^* is the one where the probabilities obtained from Eq. (21) are independent of the other parameter α_0 . Thus P_0^* is defined as

$$\left. \frac{\partial P_{I \rightarrow F}(\alpha_0, P_0)}{\partial \alpha_0} \right|_{P_0 = P_0^*} = 0 \quad (22)$$

If the product-type wavefunction is assumed, then the correlation between the two modes is not accounted for properly, i.e., quantally. It is included only in an average “classical” fashion. As mentioned the exact probabilities are independent of the two parameters above. Thus the degree of dependence we obtain with the product trial function is a measure of the amount of correlation between the two degrees of freedom.

Table I shows that the product-type wavefunction combined with a search for the optimum momentum gives results in very good agreement with the exact quantum results. We notice that the difference is small, typically less than 10% over as much as 20 orders of magnitude for various mass parameters, etc. Any difference between the exact quantum mechanical numbers and those obtained with a product-type wavefunction is, as mentioned, due to the neglect of quantum correlation. However, we see that the introduction of the variational approach almost fully corrects for

Table I. Comparison Between Variational Ehrenfest and Exact Quantum Transition Probabilities for an Atom Colliding with a Morse Oscillator with an Exponential Interaction Potential (see Refs. 6 and 7 for Details); System 1 Is a Heavy and System 2 a Light Mass Oscillator^a

Energy	Transition	Variational	Exact	Deviation (%)
System 1				
10.0	0-1	3.71(-5)	3.88(-5)	4.5
10.0	0-2	9.78(-11)	1.06(-10)	7.8
10.0	0-3	7.07(-18)	7.21(-18)	1.8
10.0	1-2	1.06(-5)	1.09(-5)	2.9
10.0	1-3	1.69(-12)	1.84(-12)	8.3
10.0	1-4	1.36(-22)	2.20(-22)	47
10.0	2-3	6.38(-7)	6.76(-7)	5.8
10.0	2-4	1.06(-16)	1.21(-16)	13
10.0	3-4	6.62(-10)	7.15(-10)	7.5
20.0	0-1	3.82(-3)	3.88(-3)	1.6
20.0	0-2	4.35(-6)	4.61(-6)	5.9
20.0	0-3	1.90(-9)	2.33(-9)	19
20.0	0-4	3.29(-13)	3.97(-13)	19
20.0	1-2	4.77(-3)	4.72(-3)	1.0
20.0	3-4	2.77(-3)	2.90(-3)	4.5
20.0	2-3	3.98(-3)	4.13(-3)	3.7
20.0	2-4	2.66(-6)	3.01(-6)	12
20.0	1-4	1.39(-9)	1.34(-9)	3.7
20.0	1-3	4.64(-6)	4.91(-6)	5.5
System 2				
5.0	0-1	1.57(-5)	1.59(-5)	1.3
9.0	0-1	1.83(-3)	1.87(-3)	2.2
9.0	1-2	1.25(-3)	1.27(-3)	1.6
13.0	0-1	1.13(-2)	1.19(-2)	5.2
13.0	1-2	1.53(-2)	1.62(-2)	5.6
13.0	1-3	4.81(-5)	5.94(-5)	20

^a The energy is given in units of $\frac{1}{2}\hbar\omega$, where ω is the oscillator frequency. The numbers in parentheses give the power of 10, i.e., $3.71(-5) = 3.71 \times 10^{-5}$.

Table II. Transition Probabilities Obtained for System 1 with Classical Initial Conditions (See Text)

Energy	Transition	Probability	Geometric mean	Exact
10.0	1 4	3.54(-15)	3.90(-20)	2.20(-22)
10.0	4 1	4.30(-25)	3.90(-20)	2.20(-22)
20.0	0-1	4.58(-3)	3.66(-3)	3.88(-3)
20.0	1 0	2.93(-3)	3.66(-3)	3.88(-3)
20.0	3 4	3.86(-3)	2.63(-3)	2.90(-3)
20.0	4 3	1.79(-3)	2.63(-3)	2.90(-3)

it. The search for the optimum momentum comes from imposing quantum boundary conditions on the system. A natural but wrong idea would be to impose classical boundary conditions. This thought would be natural due to the fact that classical equations of motion are integrated. Classical boundary conditions would be to let the initial momentum be given by

$$\frac{P_0^2}{2\mu} = E - E_I \quad (23)$$

where I is the initial state of the oscillator. We have shown for a few transitions the result of such a calculation in Table II. We notice that even the geometric mean value $\sqrt{P_{II}P_{FI}}$ is off by orders of magnitude for the weak

Table III. Comparison of the "Exact" and GWP + Correction Term Obtained with the Variational Search for the Best Momentum

System	Energy	Transition	Probability				
			"Exact"	GWP	$nc = 3$	$nc = 4$	$nc = 5$
1	10.0	0-1	3.71(-5)	3.73(-5)	3.71(-5)	3.71(-5)	3.72(-5)
1	10.0	3-4	6.62(-10)	6.96(-10)	6.59(-10)	6.64(-10)	6.84(-10)
2	9.0	0 1	1.83(-3)	1.81(-3)	1.81(-3)	1.83(-3)	1.86(-3)
2	13.0	1 3	4.81(-5)	4.54(-5)	4.54(-5)	4.69(-5)	4.79(-5)

^a nc is the maximum value of n in Eq. (30), i.e., the number of correction terms is $nc + 1$ ($nc = 3$ is the smallest number giving any correction to the GWP).

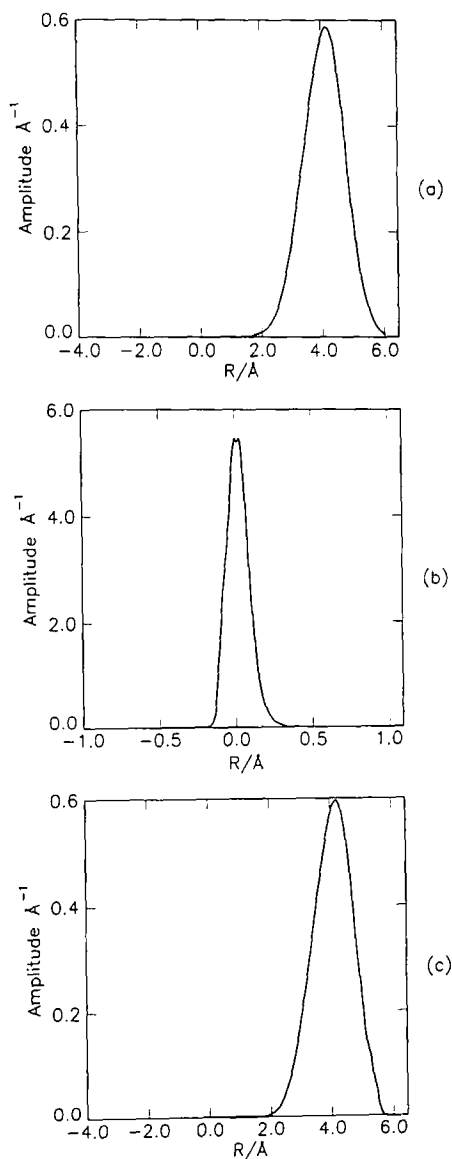


Fig. 1. The wavefunction $|X(R, t)|^2$ as a function of time for system 1. The energy is $E = 20$ and the Morse oscillator initially in the $n = 0$ state. (a) Initial Gaussian distribution ($t = 0$). (b) The distribution at the turning point for the wavepacket at $T = 7\tau$ ($\tau = 10^{-14}$ s). (c) The final distribution at $t = 14\tau$.

transitions compared to those obtained if we first introduce a search for the optimum momentum. But what is worse is that there is no theoretical justification for this choice of the classical momentum (although it is plausible). For high energies, of course, we expect P_0^* not to deviate much from either of the two possible classical values of P_0 (for the forward and reverse transitions). Traditionally the search for an optimum momentum has not been introduced in the classical path equations (discussed below). But it is known that the introduction of an average initial velocity does improve the agreement with exact calculations [2].

The variational approach to obtain P_0^* gives probabilities for which detailed balance is nearly fulfilled and the introduction of a kinematic factor (see Ref. 7) justifies the geometric mean of the forward and reverse transitions. The quantum derivation gives P_0 strictly as a parameter and it is important to notice that this is the case also if we introduce the classical path limit by assuming a Gaussian trial wave function. That is, when deriving the theory we are thinking in quantum rather than classical mechanical terms.

Figure 1 shows the wavefunction $|X(R, t)|^2$ as a function of time for system 1. We notice that it remains approximately Gaussian during the entire collision. This leads to the suggestion (as discussed above) to replace it by a Gaussian wavefunction and introduce correction terms to the Gaussian.

3. THE CLASSICAL PATH LIMIT

In order to obtain the classical path equations as the limit, we have suggested introducing the trial wavefunction as

$$X(R, t) = \Phi(R, t) \sum_{n=0} \varepsilon_n(t) (R - R(t))^n \quad (24)$$

where $\Phi(R, t)$ is a Gaussian wavepacket and the last factor is the correction wavefunction Φ_{corr} mentioned in Section 1. If one inserts this expression in the time-dependent Schrödinger equation, Eq. (8), we can get a hierarchy of equations by equating terms with the same power of $(R - R(t))^k$. In this manner we can have the TDSE fulfilled to all powers in $R - R(t)$. $R(t)$ is a reference path which is obtained by solving the classical equations of motion in an effective Ehrenfest potential; i.e., we have

$$\dot{R}(t) = \frac{P_R(t)}{\mu} \quad (25)$$

$$\dot{P}_R(t) = -\frac{\partial}{\partial R} \langle \psi | H_1^{(0)}(r, R) | \psi \rangle |_{R=R(t)} \quad (26)$$

where the brackets indicate integration over the quantum coordinate r . Furthermore, a TDSE is obtained for the r system:

$$ih \frac{\partial \psi}{\partial t} = (\hat{H}_0 + V(r, R(t))) \psi \quad (27)$$

which gives Eq. (13) if the wavefunction is expanded in the basis functions $\phi_n(r)$. Thus the above equations are the so-called classical path equations where a path $R(t)$ drives the quantum system and where the two systems are coupled self-consistently to each other through an Ehrenfest potential. Aside from the equations above we also obtain the following equations for the width parameter $A(t)$, the phase-factor $\gamma(t)$, and the correction terms $\varepsilon_n(t)$ [7]:

$$-\dot{A}(t) = \frac{1}{2} M_2 + \frac{2A(t)^2}{\mu} \quad (28)$$

$$\dot{\gamma}(t) = \frac{P(t)^2}{\mu} + \frac{ihA(t)}{\mu} \quad (29)$$

$$ih\dot{\varepsilon}_n = -\frac{2nihA(t)}{\mu} \varepsilon_n(t) - \frac{\hbar^2}{2\mu} (n+1)(n+2) \varepsilon_{n+2} + \sum_{k=0}^{n-3} \frac{M_{n-k}(t)}{(n-k)!} \varepsilon_k \quad (30)$$

where

$$M_p = \sum_{mmm} a_m^* a_n V_{mm}^{(p)} \quad (31)$$

and ε_n initially is δ_{n0} .

If we use these equations and the above mentioned variational approach, it is possible to discuss various corrections to the simple classical path theory, which involves just Eqs. (25)–(27). One is a correction which searches for the optimal momentum P_0 (initial momentum) of the reference path (as done above). This is done by projecting the wavefunction on incoming and outgoing plane waves times an internal state function for the r system. This projection is the usual one used in time-dependent scattering and can be carried out as either a space-momentum transform or a time-energy transform so as to obtain the scattering S matrix in an energy range covered by a given initial wavepacket. In quantum mechanics these S -matrix elements are independent of where the initial wavepacket is positioned in momentum space and also independent of the width of the

wavepacket. However, if the dynamics is not solved exactly as is the case in the classical path theory, then there will be a dependence on these two initial “parameters.” We have therefore previously suggested a procedure called the variational Ehrenfest procedure (or classical path method). In this method the optimal initial momentum P_0 is defined as that momentum which makes the results independent of the width parameter. This definition of the best momentum P_0 is very close to the so-called symmetrized Ehrenfest method suggested many years ago by the author [2, 8]. Aside from this correction to the classical path equations, the so-called higher-order correction terms ϵ_n can be calculated and used to improve the results [7].

We note that in the limit of many correction terms, we should approach the exact solution [to Eq. (14)]. Table III shows that, with just a few correction terms ϵ_n , we do obtain almost the “exact” values obtained with the full wavefunction $X(R, t)$. The advantage of the GWP procedure + correction is that the equations are easier to solve and that the classical equations of motion—the classical picture—are obtained as the limit of no correction. We note that the GWP approximation already gives good results and the inclusion of just a few correction terms is sufficient for obtaining the “exact” results, where by “exact,” we mean results obtained by integrating Eq. (14).

4. DISCUSSION

Although we have found a solution to all orders in ΔR , a solution which in the limit has the classical path equations, we still had to introduce the approximation, Eq. (2), in order to derive the theory. We now note that the solution is a function of the parameters P_0 , the initial momentum, and α_0 , the width parameter (the initial width or, more conveniently the width at the turning point). We then postulated that the general expansion coefficients $C_n(R, t)$ could be written as

$$\lim_{t \rightarrow \infty} C_n(R, t) = a_n(t) X(R, t; P_0^*, \alpha_0^*) \tag{32}$$

Since the correct transition probability is obtained as

$$P_{i \rightarrow j} = \frac{k_j}{k_i} \lim_{t \rightarrow \infty} \frac{|(1/\sqrt{2\pi}) \int dR \exp(ikR) C_f(R, t)|^2}{|\Psi_k^-|^2} \tag{33}$$

independent of the parameters P_0 and α_0 , we have defined the values of P_0^* and α_0^* such that

- (a) detailed balance is fulfilled, $P_{ij}(P_0^* \alpha_0^*) = P_{ji}(P_0^* \alpha_0^*)$, and
 (b) $\partial P_{ij}(\alpha_0, P_0^*) / \partial \alpha_0 = 0$,

i.e., it is possible to find a value of P_0 for which the result is independent of α_0 and where detailed balance is fulfilled. We note that the particular solution to the TDSE involves the solution of equations for the two degrees of freedom r and R , which are coupled but only in the average sense. Thus the number of equations is much smaller than and much easier to solve than the exact set of equations. Furthermore, there are several levels, from no correction to corrections involving higher-order terms and the search for optimal parameters.

In the TDSCF treatment of dynamical processes, averaging over all other degrees of freedom is introduced, when the equations of motion for a particular degree of freedom are derived. Thus this treatment includes the correlation only in some average sense. In the present semiclassical theory the idea is that a certain number (Q) of degrees of freedom—strongly coupled—are boxed together and quantum correlation is included among them. The remaining $M - Q$ degrees of freedom, where $M = 3N - 5$ (N is the number of atoms and 5 constraints comes from fixing the center of mass and conservation of total angular momentum and its projection), are treated “classically.” Correlation is included in the average (“classical”) sense both between the Q set and the $M - Q$ set and among the $M - Q$ degrees of freedom themselves. Present computer facilities set the limit for Q to about 3–4. However, large systems may conveniently be treated within the second quantization (SQ) degrees of freedom [2]. In the SQ approach the Schrödinger equation is solved in operator space and the approach is convenient for an approximate quantum description of “rigid” parts of the system as, for example, solids (bosons) or electron-hole pair excitation (fermions).

The quantum corrections to the classical path theory described above are as far as one can go in the improvement of a treatment based upon a single-configuration product trial function. It is well-known that the single configuration approach breaks down in a number of cases studied recently. They are, for example, the tunneling of a particle coupled to a heat bath [9, 10] and nonadiabatic processes [11, 12]. In such cases the obvious improvement is to introduce more than one configuration, i.e., several terms in Eq. (15). If the trial function in R -space is still a GWP, then such a theory will generate more than one “classical” trajectory. But before this is done we have demonstrated that imposing quantum boundary conditions on the single-configuration wavefunction does in fact lead to a drastic improvement of the results.

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